

Activation of ammonia dissociation by oxygen on platinum sponge studied with positron emission profiling

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Abstract

Positron emission profiling (PEP) is applied to study the adsorption and dissociation of ammonia on metallic and preoxidized platinum sponge in the temperature range 323–573 K. The results show that ammonia weakly interacts with platinum without dissociation. On the contrary, preoxidized platinum is able to dissociate ammonia. With increasing temperature more ammonia is converted into N₂, N₂O, and H₂O. Adsorbed NO appears to be an important intermediate, while its formation strongly depends on the oxygen surface coverage. Temperature-programmed experiments are performed to characterize the adsorbed nitrogen species. Furthermore, H₂, NH₃, and NO are used to react with these adsorbed nitrogen species. These experiments indicate that mainly NH_x species are present at the platinum surface.

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1. Introduction

Low-temperature selective oxidation of ammonia with oxygen, to nitrogen and water, forms a potential solution to several ammonia spills. Theoretical calculations and ultra high vacuum (UHV) experiments provided many insights in the interactions of ammonia with oxygen on platinum [1–5]. However, the adsorption of ammonia and its subsequent oxidation have not been extensively studied at atmospheric pressure. Our transient ammonia pulse experiments studied in situ with positron emission profiling (PEP) may offer valuable information on the ammonia adsorption and dissociation activated by oxygen on pure platinum catalysts. These are the first elementary steps in the low-temperature ammonia oxidation.

On clean Pt single crystals three molecular ammonia desorption states are observed, at low coverage the strongly chemisorbed ammonia desorbs around 400 K, weakly chemisorbed at 150 K, and ammonia physisorbed in the multilayer at 100 K [1,3,6–8]. Fahmi and van Santen [4]

reported for chemisorbed ammonia an adsorption energy of –108 kJ/mol based on theoretical calculations. Ammonia dissociates into nitrogen and hydrogen at temperatures above 530 K (135 kJ/mol) [3,6,9]. The ammonia dissociation can be enhanced by preadsorption of oxygen [1,3], which is explained by the fact that atomic oxygen activates the NH_x bond cleavage [4]. The various formed fragments are adsorbed on platinum in different configurations: NH₃, OH species (1-fold); NH and NH₂ adsorbates (2-fold); H, O, and N atoms (3-fold) [4]. NO preferentially adsorbs at the fcc hollow site at low coverages, at higher coverages NO additionally adsorbs on the atop site in a tilted geometry [10,11]. Oxygen molecules occupy hollow sites [12–15] whereas ammonia molecules occupy on-top sites [4,16]. The preadsorption of oxygen does not block the adsorption of ammonia [3]. The product formation of the reaction between ammonia and oxygen is dependent on the reaction conditions, i.e., pressure, reactant ratio, temperature, and the exposed Pt surface. The group of King proposed that NO is the key intermediate [3,4,17] and that the reaction pathway is dependent on the oxygen surface coverage. However, the experiments done at atmospheric pressure by Van den Broek [18] indicated that the reaction between the NH and

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the OH species is the rate-determining step. These species have also been detected at the platinum surfaces under UHV conditions [1].

A suitable technique to study in situ transient and steady-state phenomena at atmospheric pressure is positron emission profiling [19,20]. The PEP measurements offer a unique possibility of studying the various processes at the catalyst surface in a wide temperature range. PEP is a technique in which minute ($\sim 10^{-15}$ mol) quantities of radiolabeled molecules emitting positrons are injected as pulses into the feed of packed-bed reactors. The concentration distribution of radiolabeled molecules can be measured as a function of time and position within a tubular reactor bed. In this study we used ^{13}N -labeled ammonia pulses.

In this work, evidence for the activation of the ammonia adsorption and dissociation promoted by oxygen on platinum is provided by PEP pulse experiments. The conversion and product formation due to $[^{13}\text{N}]\text{NH}_3$ pulses on preoxidized platinum have been studied as a function of temperature. Here, we will demonstrate that the product selectivity is temperature dependent and that a part of the injected $[^{13}\text{N}]\text{NH}_3$ remains at the preoxidized platinum surface. In addition, the nature of the nitrogen species, which remain after the ammonia pulse on preoxidized platinum in the temperature range up to 423 K, is further investigated with temperature-programmed desorption (TPD) and temperature-programmed oxidation (TPO), and the removal of the adsorbed species by H_2 , NH_3 , and NO reaction experiments. Furthermore, we discuss the possible role of NO as a reaction intermediate.

2. Experimental

2.1. Catalytic reactor

The platinum sponge was acquired from Johnson Matthey. The sponge sample was of > 99.9% purity. The particle size of the sponge was between 250 and 350 μm and the size of the small non porous particles about 1.0–5.0 μm [18]. The amount of platinum sites calculated via BET measurement is 3.0×10^{18} sites/g and via the hydrogen chemisorption is 1.3×10^{18} sites/g. The metal surface area is determined to be 0.099 m^2/g . Atmospheric ammonia oxidation activity tests were performed in a fixed-bed reactor setup equipped with a quadrupole mass spectrometer (Balzers Instruments Omnistar GSD 3000), which was calibrated for on-line analysis of reactants and products. A quartz tube with an internal diameter of 4 mm was used as reactor. A sample of 1.8 g of pure platinum sponge was used in a catalytic bed with a length of 4.0 cm. The experiments were done at temperatures between 323 and 673 K.

Prior to a catalytic experiment the platinum sponge was reduced in situ by heating the sample in a 10 vol% H_2/He flow (40 cm^3/min) from 298 to 673 K. Subsequently the sample was kept at this temperature for 2 h. The catalyst

was then flushed with He (48 cm^3/min) for 20 min before the reaction temperature was set.

A preoxidized platinum sponge is obtained by the following treatment: the reduced catalyst was pretreated with 1 vol% O_2/He flow (48 cm^3/min) for 1 h at 373 K followed by flushing with He (48 cm^3/min) for 1 h before the reaction temperature was set. Additional $[^{15}\text{O}]\text{O}_2$ PEP experiments indicated (not shown) that on preoxidized platinum sponge oxygen is strongly bound and that oxygen adsorbs dissociatively at this temperature, which is in line with earlier reports [21–25].

2.2. Positron emission profiling

The ^{13}N nucleus emits a positron upon decay. Positron emission profiling is based on the detection of the two 511 keV gamma photons which originate from the annihilation of this positron with an electron. These two 511 keV gamma photons are simultaneously emitted in opposite directions and they travel typically a few centimeters in solid matters. Coincidental detection of two photons by scintillation detectors (BGO) provides the position of the annihilation. In practice, the tubular reactor is horizontally placed between two arrays (upper and lower) of nine scintillation detectors. In both arrays the detectors were tightly placed, which results in the spatial resolution of 2.9 mm. The average concentration of all radiolabeled molecules within a certain volume (length 2.9 mm) is measured at time intervals of 0.5 s. The measurement of radiolabeled molecules is simultaneous over the total detection length (5 cm), thus within the 17 vol segments. In this way the concentration distribution of the positron emitting molecules can be measured as a function of position and time [19,29].

The Eindhoven 30 MeV cyclotron was used to irradiate a water target with highly energetic protons of 16 MeV. The irradiation time was 10 min and a typical beam current of 500 nA was used. The target was a flowthrough water target, with a total volume of 7 ml containing a dual foil (Duratherm 600, thickness 15 μm). In this way formed $[^{13}\text{N}]\text{nitrate}$ and $[^{13}\text{N}]\text{nitrite}$ were subsequently reduced to $^{13}\text{NH}_3$, using DeVarda's alloy method [26,27]. The production method of gaseous pulses of $[^{13}\text{N}]\text{NH}_3$ was described elsewhere [28]. A pulse time of 10 s was used to inject a mix of $^{13}\text{NH}_3/^{14}\text{NH}_3$ into the reactant stream, henceforth indicated as $[^{13}\text{N}]\text{NH}_3$. In this way $^{14}\text{NH}_3$ ($\sim 10^{-5}$ mol) was measured with the mass spectrometer and $^{13}\text{NH}_3$ ($\sim 10^{-15}$ mol) was monitored with PEP. Since the $^{13}\text{NH}_3$ concentration varies in each pulse, the absolute concentration of radiolabeled molecules in the various experiments cannot be directly compared. However, the labeled species are either introduced in a large flow of nonlabeled ammonia or as trace amounts in ammonia-free flows. As such, these variations will not affect the results between the various experiments.

2.3. PEP pulse experiments

The reduced platinum catalyst was kept under a flow ($48 \text{ cm}^3/\text{min}$) of 1.0 vol% ammonia/helium or 1.0 vol% oxygen/helium or He flow at 273–573 K. Subsequently, a pulse of $[^{13}\text{N}]\text{NH}_3$ was injected in this ammonia/helium or oxygen/helium flow or helium flow. A gas hourly space velocity (GHSV) of 5700 h^{-1} is mostly used. The $[^{13}\text{N}]\text{NH}_3$ pulse experiments were performed over the platinum and preoxidized platinum sponge in a similar manner. In each PEP experiment mass spectrometry was used to simultaneously monitor the effluent products.

2.4. Temperature-programmed experiments

Temperature-programmed experiments were performed exactly 170 s (TPD) or 100 s (TPO) after the injection of a pulse of $[^{13}\text{N}]\text{NH}_3$ in He flow of $40 \text{ cm}^3/\text{min}$ (GHSV = 5700 h^{-1}) at 373 K over the preoxidized platinum catalyst. The temperature was raised with 10 K/min ($40 \text{ cm}^3/\text{min}$) under He (TPD) or 1.0 vol% O_2/He (TPO) flow.

2.5. Removal of adsorbed species by H_2 , NH_3 , and NO

The reaction experiments were performed more than 300 s after the injection of a pulse of $[^{13}\text{N}]\text{NH}_3$ in He flow of $48 \text{ cm}^3/\text{min}$ (GHSV = 5700 h^{-1}) over the preoxidized platinum catalyst at 323–348 K. In these experiments the He carrier flow was replaced by either 1.0 vol% NH_3/He or 4.0 vol% H_2/He or 0.5 vol% NO/He flow ($48 \text{ cm}^3/\text{min}$).

3. Results and discussion

3.1. Ammonia adsorption and dissociation on platinum and preoxidized platinum

3.1.1. Activation of ammonia adsorption by oxygen

Fig. 1A shows that an injected radiolabeled ammonia pulse into a NH_3/He flow (323 K) travels through the platinum catalyst bed. The retention time of $[^{13}\text{N}]\text{NH}_3$ through the catalyst bed was approximately 9 s. This is longer than the retention time of He (less than a second). At higher temperatures this ammonia retention time decreases, giving a value of 5 s at 423 K. Judging from the absence of broadening of the pulse, we expect that diffusion limitations of ammonia in the sponge material are negligible [30]. Fig. 1A shows that the ammonia adsorption equilibrium is fast and indicates a weak molecular adsorption of ammonia.

The injection of $[^{13}\text{N}]\text{NH}_3$ into an ammonia-free He flow over the reduced platinum sponge (Fig. 1B) clearly shows that injected ammonia also travels through the catalyst bed in this case. Gas-phase analysis showed that only NH_3 is detected at the reactor outlet, which indicates that ammonia does not dissociate under these conditions which is in line with earlier reports [1,2,31]. Therefore, we conclude that the

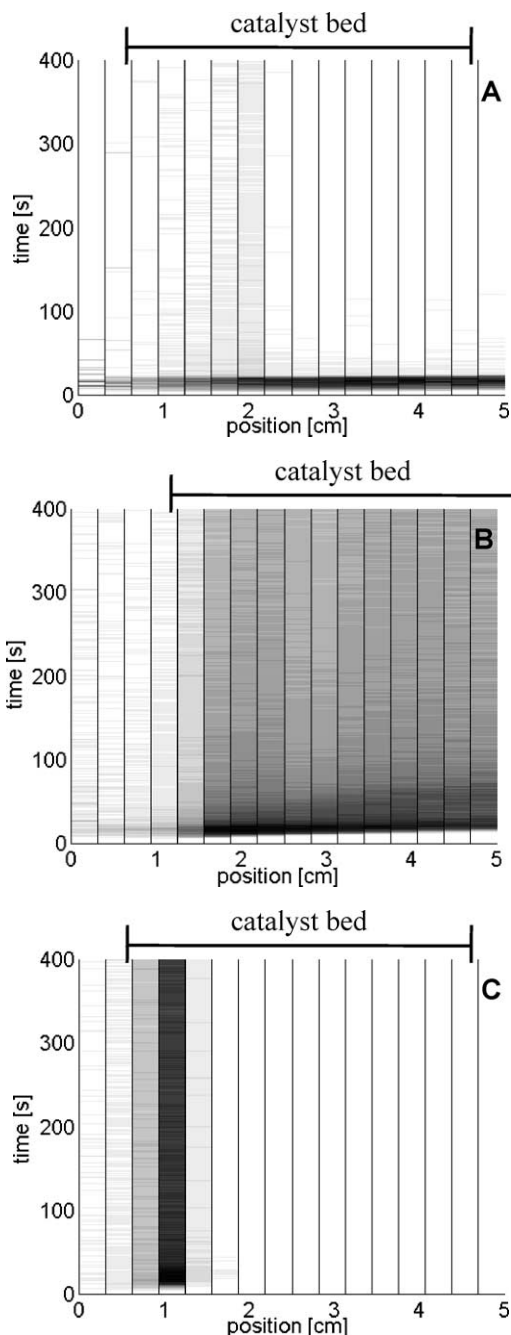


Fig. 1. PEP image of a pulse injection of $[^{13}\text{N}]\text{NH}_3$ at 323 K (A) in a 1 vol% NH_3/He flow ($48 \text{ cm}^3/\text{min}$) on Pt sponge; (B) in He flow ($48 \text{ cm}^3/\text{min}$) on Pt sponge; (C) in He flow ($48 \text{ cm}^3/\text{min}$) on the preoxidized Pt sponge. The color intensity represents the concentration of $^{13}\text{NH}_3$ (dark = high concentration).

PEP image shows the weak binding of ammonia on platinum. A relatively small amount of the labeled ammonia species (15%) remained adsorbed at the platinum surface. This adsorption is most probably caused by the incomplete reduction of the platinum surface.

The in situ PEP technique allows visualization of the promoting effect of oxygen in ammonia adsorption and dissociation. In contrast to Fig. 1B, the adsorption of ammonia

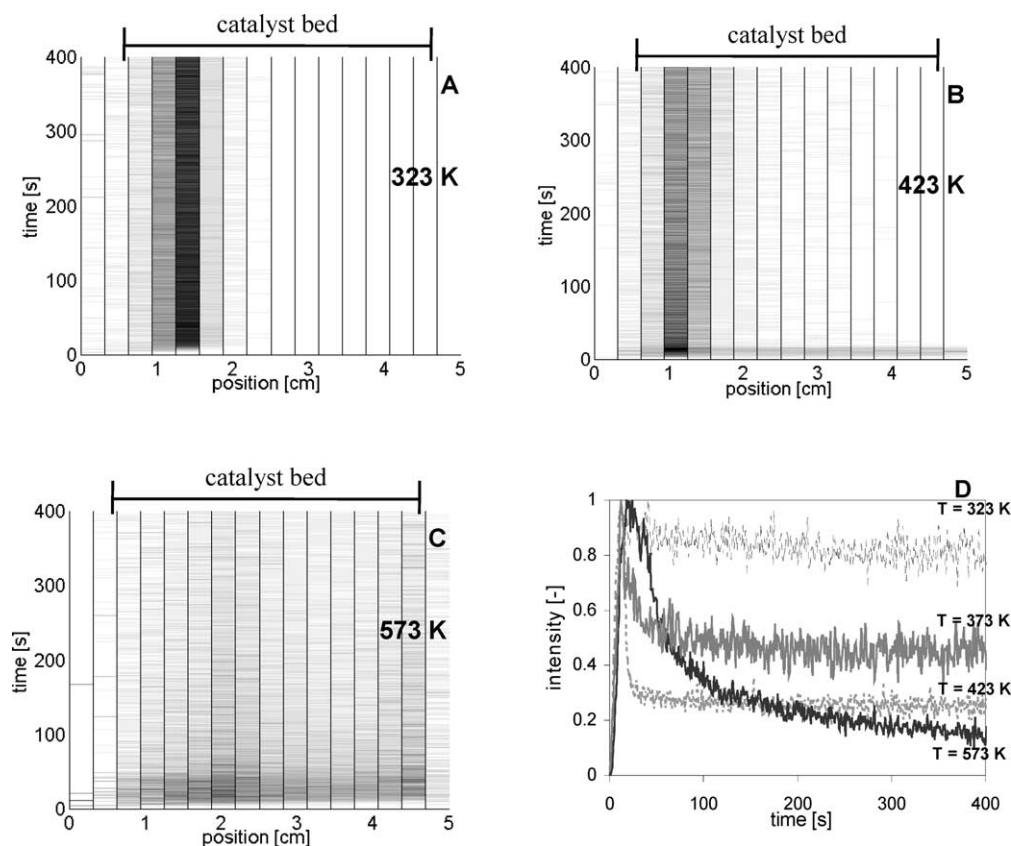
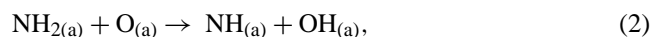


Fig. 2. PEP images of an pulse injection of $[^{13}\text{N}]\text{NH}_3$ in 1.0 vol% O_2/He flow ($48\text{ cm}^3/\text{min}$) on preoxidized Pt sponge at (A) 323, (B) 423, and (C) 573 K; (D) integrated ^{13}N concentration as function of time for presented temperatures. The color intensity represents the concentration of $^{13}\text{NH}_3$.

on the preoxidized surface (Fig. 1C) is strong. The ^{13}N species are adsorbed already at the beginning of the catalyst bed and do not desorb from the surface during the experiment. This indicates that the presence of oxygen leads to enhanced dissociation of ammonia on Pt. This agrees with recent calculations performed by Fahmi and van Santen [4], who calculated that adsorbed atomic oxygen activates the N–H bond cleavage. Accordingly, we propose the following mechanism for the NH_3 conversion:



As we did not detect dinitrogen at the relatively low temperature of 323 K, we expect that atomic nitrogen is not formed. However, due to the high surface coverage of the various species (OH, NH_2 , NH, NO, N) diffusion may be impaired, thereby hindering reconstruction to N_2 .

In paragraphs 2 and 3 the nature of these adsorbed species is investigated. The role of NO in the product formation is mainly addressed in paragraph 3. First, we present the influence of the temperature on the ammonia dissociation on the preoxidized platinum sponge.

3.1.2. Influence of temperature on the ammonia dissociation on preoxidized Pt

The PEP images of the radiolabeled ammonia pulses on preoxidized platinum change significantly with increasing temperature. Fig. 2 shows the PEP images of $[^{13}\text{N}]\text{NH}_3$ pulses over preoxidized platinum in an oxygen flow in the temperature range of 323–573 K including the integrated ^{13}N concentration in the reactor at different temperatures as a function of time. At 323 K almost no gaseous products are formed and the total concentration of ^{13}N remains at the catalyst (Figs. 2A and 2D). Below 423 K the PEP images are very similar and the ^{13}N concentration is observed at the beginning of the catalyst bed and the total radioactivity profile (Fig. 2D) shows a sharp decrease as gaseous products are formed. The decrease of the ^{13}N concentration at 423 K is due to the formation of nitrogen and some nitrous oxide. Fig. 3A provides evidence for the formation of N_2 and N_2O by MS analysis. These products evolve simultaneously as a response to the $^{14}\text{NH}_3/^{13}\text{NH}_3$ pulse. The water formation is detected with an obvious delay compared to N_2 and N_2O evolution. This stems from the stronger interaction of these water molecules with the catalytic surface. As can be observed when comparing Figs. 3A and 3B this adsorption of water is less pronounced at higher temperatures. At a temperature of 573 K the PEP image is substantially changed (Fig. 2C). A reaction zone is still observed at the

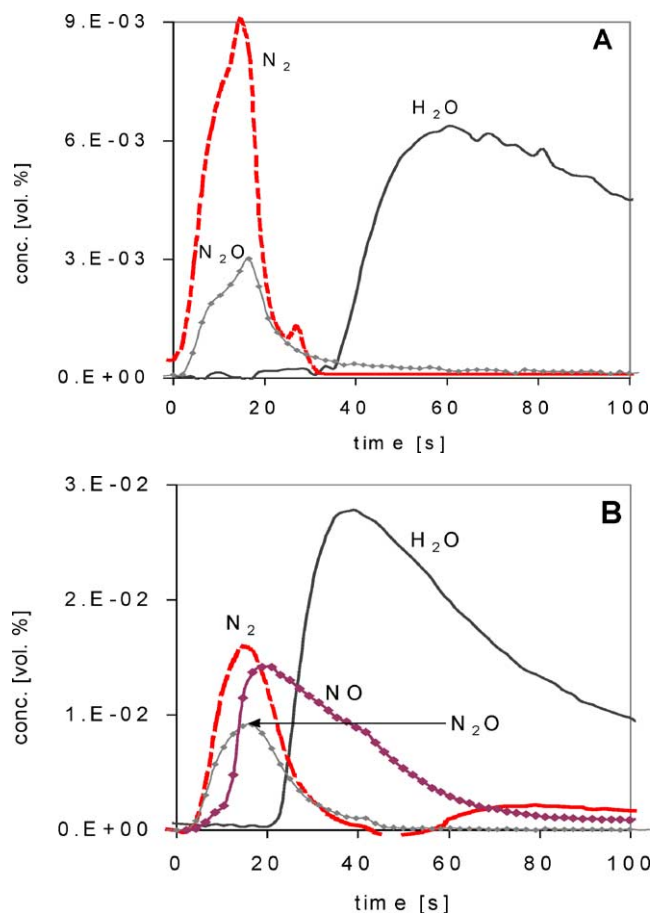
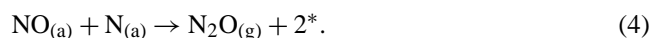


Fig. 3. Formation of N₂, N₂O, NO, and H₂O measured by online mass spectrometry on a response of [¹³N]NH₃ injection in 1 vol% O₂/He flow (48 cm³/min) on the preoxidized Pt sponge at (A) 423 and (B) at 573 K.

beginning of the catalyst bed, but in contrast to the observation at 423 K not all the products leave the catalyst bed directly. The formation of NO explains the changes in the PEP image, because NO readsorbs at the platinum surface throughout the catalyst bed. This is not the case for N₂ and N₂O, which have a very low adsorption constant. Consistently, Fig. 2D shows a relatively slow decrease of the ¹³N concentration from the catalyst due to the NO readsorption. At this relatively high temperature almost all injected ammonia reacts and forms gaseous products as shown in Fig. 2D.

In conclusion, the results indicate that the relatively high oxygen coverage on platinum promotes NO_(a) formation. At low temperatures NO_(a) leads to N₂O via



However, at temperatures higher than 573 K the NO surface coverage is low, due to desorption of NO, resulting in a lower N₂O formation. The formation of nitrogen is assumed to proceed via atomic nitrogen originating from NH_x species rather than via the dissociation of NO_(a). The dissociation of NO_(a) at low temperature (< 400 K) and also in the situation of a high adsorbate coverage is unfavorable [2,32–34].

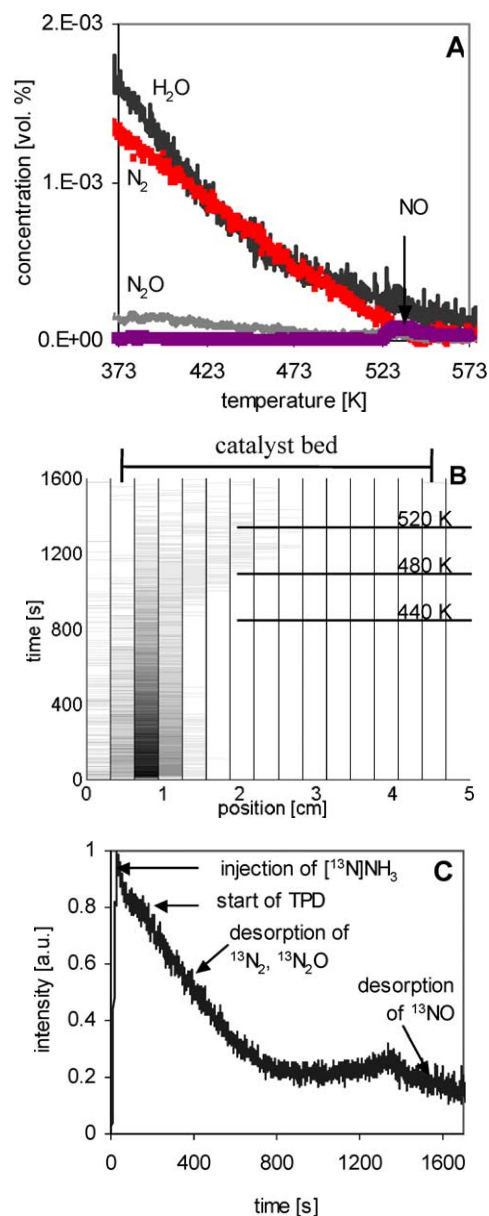


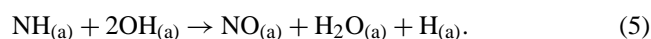
Fig. 4. A [¹³N]NH₃ pulse was adsorbed on the preoxidized platinum sponge kept under He flow (40 cm³/min) at 373 K followed after 170 s by a temperature-programmed desorption experiment: (A) TPD spectrum; (B) PEP image, the color intensity represents the concentration of ¹³NH₃; (C) normalized concentration as function of time ($T = 373\text{--}573$ K, 10 K/min, He flow of 40 cm³/min).

3.2. Temperature-programmed measurements

3.2.1. Temperature-programmed desorption

In this experiment the temperature is raised from 373 to 573 K after injection of a [¹³N]NH₃ pulse on the catalyst at 373 K (Fig. 4). The observed background of the MS signals of the products are relatively high since the catalyst could not be sufficiently flushed with He before starting a TPD experiment due to a relatively fast ¹³N decay. The desorption of the inert N₂ and N₂O molecules is qualitatively observed in the PEP images (Fig. 4C). The signal of the in-

egrated ^{13}N concentration decreases at the same time as N_2 and N_2O desorb. The desorption of N_2 and N_2O continues up to 480 K, because at that temperature the total radioactivity profile (Fig. 4C, from 800 s) shows no further decrease of the ^{13}N concentration. N_2 and N_2O have low adsorption constants [35,36], meaning that were not present at first but are formed during the TPD experiment. The formation of N_2O is assigned to reaction (4). Since radiolabeled ammonia was injected on the preoxidized surface the oxygen coverage is relatively high and therefore the dissociation of NO on platinum is unfavorable. This leads to the assumption that $\text{N}_{(\text{a})}$ species originate from adsorbed NH_x species. Another important feature that supports the presence of the NH_x species on the surface is substantial formation of water, which is found to be accompanied by the N_2 and N_2O formation. $\text{NO}_{(\text{a})}$ needed for the N_2O formation originates from NH_x species:



At lower temperatures $\text{NO}_{(\text{a})}$ does not dissociate and is preferentially converted into N_2O .

Above 480 K about 20% of ^{13}N is still adsorbed at the platinum surface (Fig. 4C, at 800 s). In fact the ^{13}N integrated concentration profile should change to a horizontal line, but the radioactivity profile slightly increases. This is caused by spreading of the radioactive compound through the catalyst bed, while the total amount of labeled species in the reactor remains constant. When all these species are concentrated in the first part of the reactor and thus at the edge of the surrounding detector, the detection efficiency of the total amount of radioactive material is somewhat less than when it would be concentrated in the middle. This mainly affects the integrated profiles and not the PEP plots that show the radioactive concentration for each position as function of time. This profile of total radioactivity increase must be taken into account only in the TPD or TPO experiments and especially when the still high concentration of the adsorbed ^{13}N spreads from one position to subsequent positions. Still, the qualitative value of 20% is correct, because this value is in accordance with the value found in the radioactivity profile of the first position in the catalyst bed, which is not affected by the above-described artifact. After the temperature has reached 520 K the total radioactivity profile (Fig. 4C) decreases for the second time. The PEP image (Fig. 4B) shows that the ^{13}N concentration is slowly moving through the catalyst bed, indicating that readsorption is taking place. The velocity of the ^{13}N moving through the catalyst bed is not linear because the desorption is enhanced by the increasing temperature. Thus the ^{13}N transport through the reactor is accelerated in time. At the moment that the activity reaches the end of the catalyst bed ($T = 520$ K) only NO is detected with MS. For that reason the desorption of ^{13}N is assigned to ^{13}NO . In ultrahigh vacuum experiments on single crystals the energy for NO desorption is found to be around 150 kJ/mol [2,37,38] and NO desorbs at temperatures around 400 K. In our experiment, the PEP image

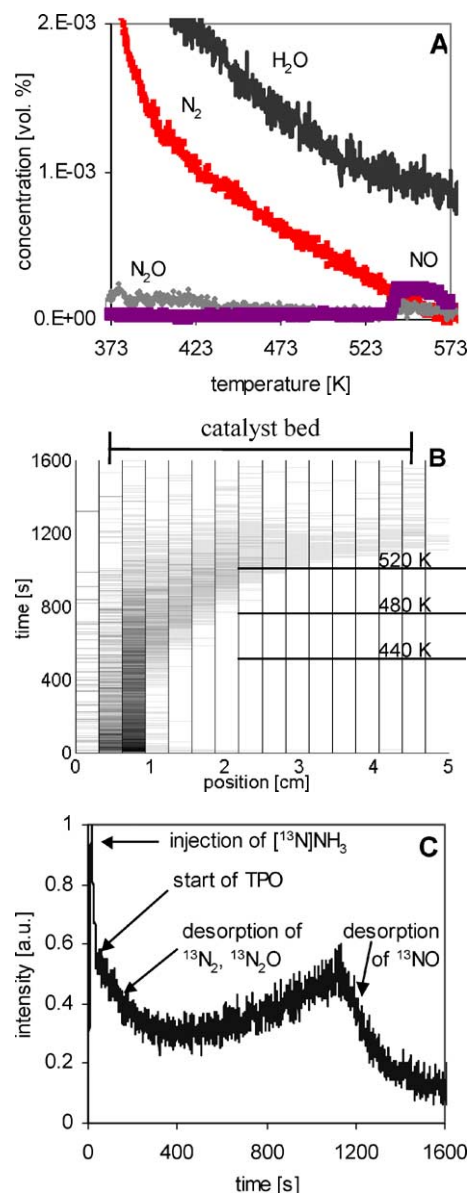


Fig. 5. A ^{13}N pulse was adsorbed on the preoxidized platinum sponge kept under He flow ($40\text{ cm}^3/\text{min}$) at 373 K followed after 100 s by a temperature-programmed oxidation experiment: (A) TPO spectrum; (B) PEP image, the color intensity represents the concentration of ^{13}N ; (C) normalized concentration as function of time ($T = 373\text{--}573$ K, $10\text{ K}/\text{min}$, $1\text{ vol}\% \text{ O}_2/\text{He}$ flow of $40\text{ cm}^3/\text{min}$).

shows that NO starts to desorb (moves to subsequent positions) around 440 K.

3.2.2. Temperature-programmed oxidation

In this experiment a ^{13}N pulse was adsorbed on the preoxidized platinum sponge kept under He flow at 373 K, and then the temperature is raised from 373 to 573 K in $1\text{ vol}\% \text{ O}_2/\text{He}$ flow of $40\text{ cm}^3/\text{min}$ (Fig. 5). The results from TPO experiments are in qualitative agreement with those of TPD experiments. In the first minutes of the TPO experiment (up to 423 K) ^{13}N species desorb, which can be observed in Fig. 5C as the integrated ^{13}N concentration

slowly decreases. This ^{13}N desorption is assigned mainly to nitrogen formation (Fig. 5A). The background signal of the measurement for nitrogen and water is high and therefore quantitative interpretation is not possible. Hardly any N_2O is formed, which is in contrast with the TPD experiment. Fig. 5C shows that the nitrogen desorption ends at 400 s from the start of the experiment, which corresponds in Fig. 5A to a temperature of 420 K. At that temperature, 30% of the injected ^{13}N is still present at the surface. As noted before, the increase in radioactivity is due to a detector artifact. Fig. 5A shows that in the presence of gas-phase oxygen, NO is the major species desorbing at 540 K. The actual desorption temperature of NO is 440 K, since at this temperature the ^{13}N concentration starts to move in the catalyst bed. In comparison with the TPD experiment NO desorbs at a similar temperature, which is not surprising because in both experiments platinum was precovered with oxygen. In correspondence with Fig. 4B, Fig. 5B shows that equilibrium of ^{13}NO species is controlled by the readsorption on the platinum surface. As already noted the NO transport is accelerated with increasing temperature. In this TPO experiment all adsorbed ^{13}N species are removed.

The increase of the temperature up to 400 K activates the bond cleavage of NH_x by atomic oxygen according to reactions (2) and (3). Again, the formation of nitrogen is assumed to proceed via recombination of atomic nitrogen. At high oxygen surface coverage NO can be formed via



Although desorption of NO is favorable above 400 K, NO formation occurs already at lower temperatures [2]. This can also be observed indirectly in our experiment. Nitrogen is largely desorbed at 420 K; however, still some ^{13}N species are retained at the surface. Obviously, above 420 K the $\text{NH}_x + \text{O}_{(\text{a})}$ reaction does not proceed, and nitrogen is not produced, which suggests the absence of NH_x species on the surface. On the other hand, the formation of NO explains the retained ^{13}N species. NO is unreactive with respect to oxygen and it will remain adsorbed on platinum till the desorption enthalpy is overcome.

3.3. Reaction of adsorbed N species with H_2 , NH_3 , and NO

3.3.1. Reaction with hydrogen

A ^{13}N pulse was adsorbed on a preoxidized platinum sponge kept under He flow at 348 K followed by a removal of the adsorbed species with hydrogen (Fig. 6). Fig. 6A shows that the replacement of He by H_2 results in N_2O , N_2 , and H_2O formation. It is clear from Figs. 6B and 6C that almost all adsorbed nitrogen species are removed from the platinum surface in the presence of H_2 . This means that the activation energies for the surface reactions to form N_2O and N_2 are relatively low, since already at 348 K all nitrogen species are removed. It is assumed that

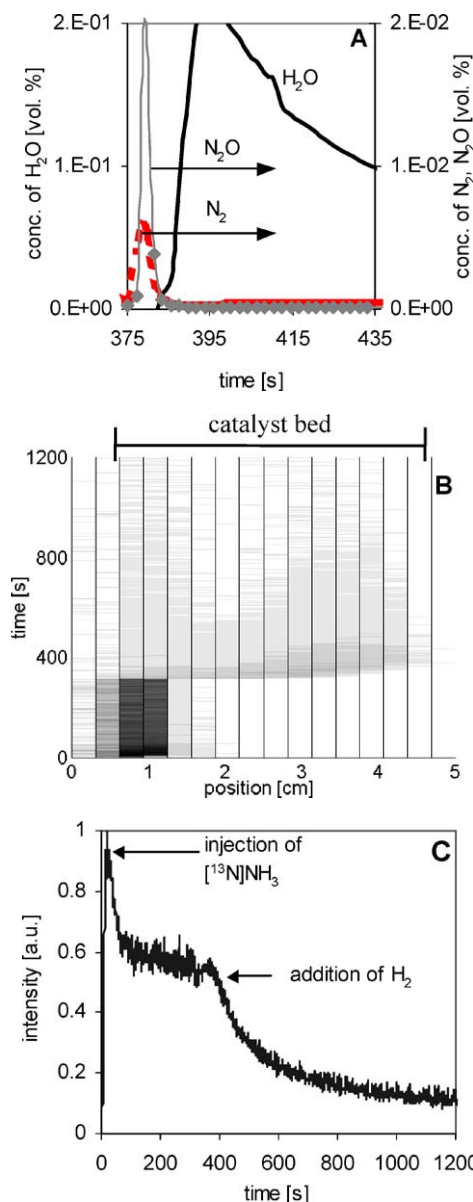
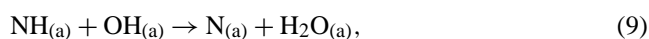
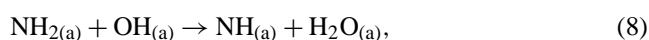
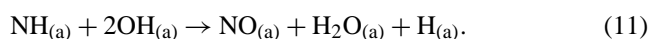


Fig. 6. A ^{13}N pulse was adsorbed on a preoxidized platinum sponge kept under He flow ($48 \text{ cm}^3/\text{min}$) followed after 380 s by a removal of N species with hydrogen: (A) MS spectrum, shown from the moment of H_2 addition; (B) PEP image, the color intensity represents the concentration of $^{13}\text{NH}_3$; (C) normalized concentration as function of time ($T = 348 \text{ K}$, 10 vol% H_2/He flow of $48 \text{ cm}^3/\text{min}$).

hydrogen first reacts with oxygen forming hydroxyl groups. OH groups do not only form water but they also react with the adsorbed NH_x species to produce N_2 :



However, higher OH concentrations favor the formation of NO:



NO cannot desorb at this low temperature. Instead it reacts with $N_{(a)}$ to form N_2O . NO could also be an intermediate leading to N_2 formation:



However, this reaction can only occur at relatively low oxygen surface coverage because the nitrogen/oxygen bond of NO needs to be broken. For that reason this route of the nitrogen formation can be activated after the initial desorption of N_2O and H_2O from the surface. Eventually, platinum is reduced and the oxygen surface coverage is lowered.

3.3.2. Reaction with ammonia

In this experiment, a $[^{13}N]NH_3$ pulse was adsorbed on the preoxidized platinum sponge kept under He flow at 348 K, followed by a removal of the adsorbed species with ammonia (Fig. 7). Upon addition of ammonia to the He flow N_2 , N_2O , and H_2O are observed at the reactor outlet (Fig. 7A). Figs. 7B, and 7C show that all ^{13}N species are instantaneously removed from the surface. Similar to the hydrogen experiment, OH groups are produced followed by the desorption of water. These hydroxyl groups also react with $^{13}NH_x$ species to form adsorbed NO and eventually dinitrogen. The amount of N_2O formed is much lower than the amount of N_2 , although it agrees well with the amount formed in the hydrogen experiment. In contrast to nitrogen and water, N_2O is only formed in the first seconds after the replacement of He by the ammonia flow. This suggests that in the beginning of the ammonia addition $NO_{(a)}$ is formed, which is similar to the observations with the H_2 flush experiment. Obviously, nitrogen and water are not only produced from the adsorbed ^{13}N species, but mainly originate from gas-phase ammonia. The addition of ammonia results in a high concentration of the nitrogen-containing species on the platinum surface. The high concentration of ammonia favors selective N_2 formation, which is also observed in UHV experiments [2,6]. The production of N_2 and H_2O decreases in time because less oxygen is available for the reaction. This results in an oxygen-free surface, which is confirmed by measuring an additional PEP image after a $[^{13}N]NH_3$ pulse in this ammonia flow (not shown). This image was identical to Fig. 1A showing the equilibrium of ammonia on platinum.

3.3.3. Reaction with NO

The role of NO as a reaction intermediate is further investigated in an experiment, in which a $[^{13}N]NH_3$ pulse was adsorbed on the preoxidized platinum sponge kept under He flow at 323 K, followed by a removal of the adsorbed species with nitric oxide (Fig. 8). Figs. 8B, and 8C show that upon addition of an NO flow about 50% of the ^{13}N species are instantaneously removed from the platinum surface. This partial conversion has two possible explanations. First, due to inaccessibility or a high surface coverage, NO does not react with all of the adsorbed ^{13}N species. This explanation is in contrast with the experiments with hydrogen and ammonia, where all ^{13}N species were removed. Thus

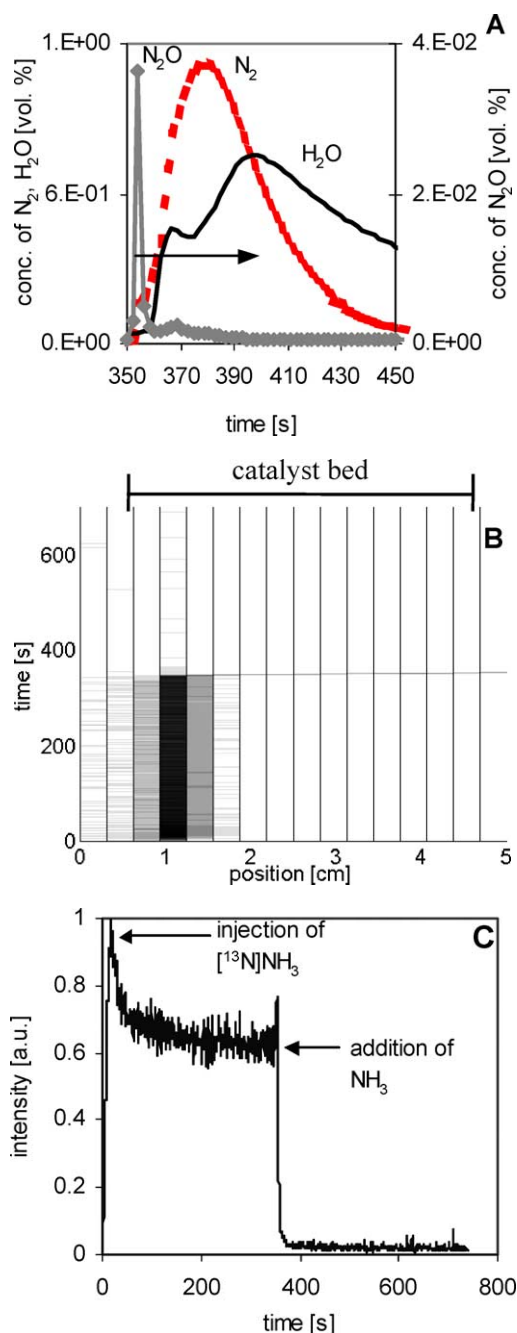


Fig. 7. A $[^{13}N]NH_3$ pulse was adsorbed on the preoxidized platinum sponge kept under He flow ($48 \text{ cm}^3/\text{min}$) followed after 350 s by a removal of N species with ammonia: (A) MS spectrum, shown from the moment of NH_3 addition; (B) PEP image, the color intensity represents the concentration of $^{13}NH_3$; (C) normalized concentration as function of time ($T = 348 \text{ K}$, 1.0 vol% NH_3/He flow of $48 \text{ cm}^3/\text{min}$).

the effect of the high surface coverage most probably can be excluded even though NO preferably adsorbs on the same sites as oxygen (hollow sites), while ammonia adsorbs on the atop sites. The second explanation is that NO selectively reacts with one of the adsorbed ^{13}N species. Only N_2O is formed as a result of the NO flush (Fig. 8A). High oxygen surface coverage, together with high partial pressure of

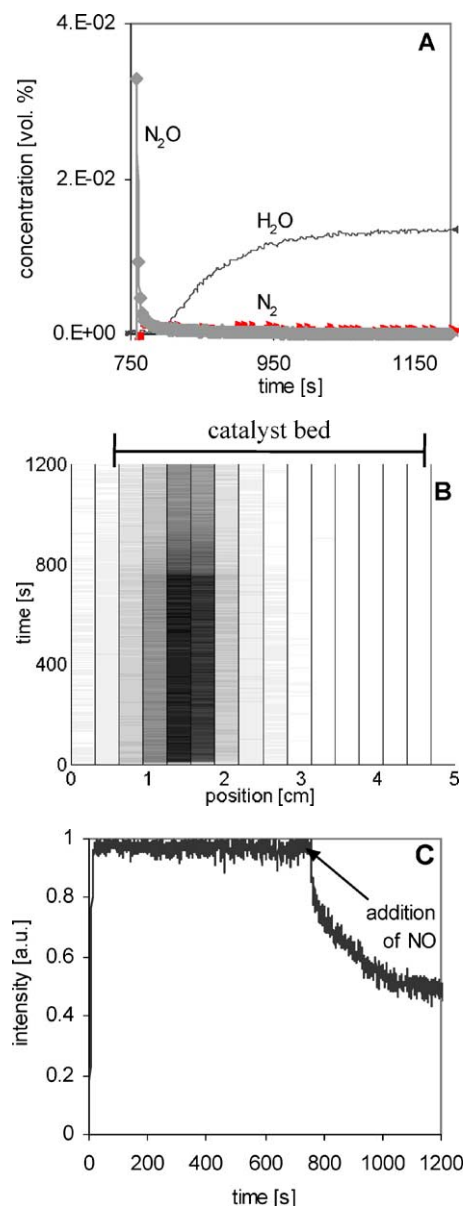
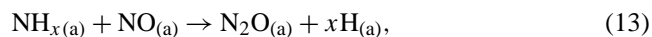


Fig. 8. A [¹³N]NH₃ pulse was adsorbed on the preoxidized platinum sponge kept under He flow (48 cm³/min) followed after 750 s by a removal of N species with nitric oxide: (A) MS spectrum, shown from the moment of NO addition; (B) PEP image, the color intensity represents the concentration of ¹³NH₃; (C) normalized concentration as function of time ($T = 323$ K, 0.5 vol% NO/He flow of 48 cm³/min).

NO, favors the formation of N₂O above N₂. Temperature-programmed experiments and ammonia and hydrogen flush experiments suggested that the adsorbed ¹³N species are ¹³NH_x. It is plausible that NO selectively reacts with one of these species:



The abstraction of one hydrogen from NH_(a) by NO giving N₂O_(a) is more probable, because NH₂ would lead to H₂, which is not detected with MS.

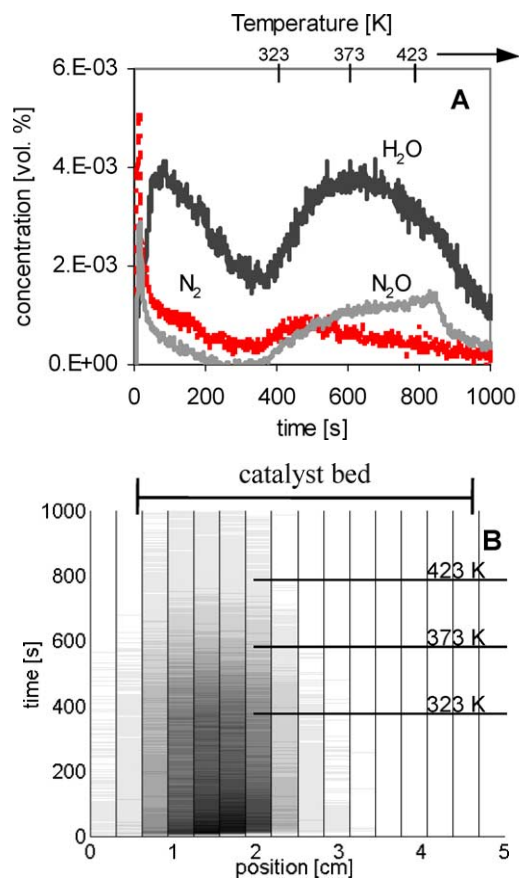


Fig. 9. A [¹³N]NH₃ pulse was injected on the preoxidized platinum sponge kept under NO/He flow at 323 K. After 400 s temperature was increased with 15 K/min (A) MS spectrum; (B) PEP image, the color intensity represents the concentration of ¹³NH₃ (0.5 vol% NO/He flow of 48 cm³/min).

Injecting an additional pulse of [¹³N]NH₃ in the NO flow, under the same reaction conditions, 40 min after the first pulse (Fig. 9) showed that on the platinum surface covered with O_(a) and NO_(a) the adsorption of ammonia is not prohibited. [¹³N]NH₃ directly reacts at the beginning of the catalyst bed, but in contrast to the first pulse (Fig. 8), now 80% of the injected ¹³N is retained at the surface. The second difference is the formation of N₂ in addition to N₂O. This [¹³N]NH₃ pulse also leads to water formation and thus to reduction of platinum. Since the oxygen surface coverage is lowered, dinitrogen formation becomes more favorable, which was also observed in the hydrogen and ammonia reaction experiments. By increasing the temperature the remaining ¹³N species desorb from the surface as N₂ and N₂O (Fig. 9A). The desorption of nitrogen and nitrous oxide is again accompanied by water formation/desorption, indicating that mainly the NH_x species are present at the surface. Both desorption peaks cease, which actually means that NO at this temperature does not decompose at the surface, which is confirmed in another experiment, in which temperatures up to 623 K were needed to observe production of nitrogen and oxygen from NO. The ¹³N species are already removed from the surface at 573 K and thus ¹³NO does not remain at the sur-

face. These NO flush experiments suggest that ^{13}NO was not formed in large amounts at the surface and that the $[^{13}\text{N}]\text{NH}_3$ pulse in the ^{14}NO flow at the preoxidized platinum surface leads to $^{13}\text{NH}_x$. Thus the formation of N_2O and N_2 is due to the reaction of $\text{NH}_{x(a)}$ with $^{14}\text{NO}_{(a)}$, $\text{O}_{(a)}$, and $\text{OH}_{(a)}$.

3.4. General discussion

Our PEP results clearly demonstrate that ammonia readily dissociates in the presence of coadsorbed oxygen. At low temperatures ammonia does not dissociate on the pure platinum sponge and the adsorption of ammonia is weak. Obviously, the presence of atomic oxygen decreases the activation barrier for the ammonia dissociation. Mechanistically, we envisage that oxygen atoms readily abstract hydrogen from coadsorbed ammonia. Our results also suggest that oxygen and ammonia occupy different adsorption sites. Schematically,

adsorption of NH_3 on $\text{Pt}_{\text{reduced}} \rightarrow$ weak molecular ads.;

adsorption of NH_3 on $\text{Pt}-\text{O} \rightarrow$ strong dissociative ads.

The radiolabeled PEP experiments have shown that the preadsorbed oxygen favors the dissociation of ammonia, which leads to production of N_2 , N_2O , and NO . The product selectivity strongly depends on the temperature. It has been shown that below 423 K mainly nitrogen and nitrous oxide were formed and above this temperature also NO . The PEP experiments indicate that all ammonia reacts at the beginning of the catalyst bed and that $[^{13}\text{N}]\text{NH}_3$ is partly converted into gaseous products and partly remains adsorbed at the surface in some dissociated form. Temperature-programmed experiments indicate that the remaining adsorbed species at the surface are mainly NH_x species because the formation of nitrogen and nitrous oxide is accompanied by the production of a large amount of water. The NO reaction experiment provides further indications that NH_x species remain at the surface. Thus, upon adsorption of ammonia hydrogen atoms are stripped off by adsorbed oxygen species. These exothermic reactions, consecutively lead to the formation of atomic nitrogen and OH groups. Fahmi and van Santen [4] showed that NH bond scissioning is energetically more costly than that of NH_2 and that the recombination of atomic nitrogen is not the rate-determining step. Our experiments are performed at relatively low temperature. The relatively high-surface coverages also contribute to the blocking of certain surface reaction pathways on the surface.

As already noted a part of $[^{13}\text{N}]\text{NH}_3$ reacts toward N_2 , N_2O , and NO . A simplified model of the reaction mechanism includes formation of atomic nitrogen, which leads to nitrogen and nitrous oxide (below 423 K). OH groups form water and also promote the formation of $\text{NO}_{(a)}$ via the reaction with NH_x . At high oxygen surface coverage and below 350 K the formation of nitrogen from NO dissociation is not favorable [2]. Therefore, it is concluded that atomic nitrogen is formed from the abstraction of hydrogen from the

NH_x species. The formed NO also cannot desorb at these low temperatures and therefore under these conditions N_2O is selectively formed. A known route for the formation of N_2O is the reaction between $\text{N}_{(a)}$ with $\text{NO}_{(a)}$. The reaction experiment with NO also indicated another possibility, in which NO selectively reacts with $\text{NH}_{(a)}$ to form N_2O , even at 323 K. The formation of nitrogen becomes more favorable at lower oxygen surface coverage, which is shown in the hydrogen and ammonia reaction experiments. Above 440 K the TPD and TPO experiments nicely indicate that NO desorbs from a preoxidized platinum surface. Since at higher temperatures NO desorption is possible, the selectivity toward N_2O decreases in favor of the NO production, as shown in Fig. 3B. An interesting feature of the NO desorption from platinum is the readsorption, which was distinctively observed in the PEP images.

4. Conclusions

The experiments have shown that dissociation of ammonia on platinum is not favorable and that the interaction of ammonia with platinum is weak at 323 K. This study, performed under atmospheric pressure conditions, confirms UHV and theoretical studies proving that ammonia dissociation on platinum is activated by the presence of oxygen at the surface. The experiments elegantly show that a platinum surface precovered with oxygen initiates the ammonia dissociation leading to the gaseous nitrogen-containing products. Ammonia dissociation on a preoxidized platinum surface was further investigated as a function of temperature. At temperatures below 423 K the pulse experiments resulted in the formation of mainly nitrogen and a small amount of N_2O . Above 423 K the product selectivity is changed and also NO is formed. It was observed with PEP that ammonia reacts at the beginning of the catalyst bed and that a part of $[^{13}\text{N}]\text{NH}_3$ remained at the surface as ^{13}N species. The TPD and TPO experiments together with the reaction with hydrogen, ammonia, and nitric oxide experiments indicated that mainly NH_x species are present at the surface. However, NO is an important reaction intermediate. In an oxygen-rich environment the NO formation leads to N_2O and with temperatures above 423 K gaseous NO is detected. The NO flush experiments indicated that NO selectively reacts with the NH species to form N_2O . Nitrogen is preferably formed at the lower oxygen surface coverage.

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